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RESEARCH ARTICLE

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Behavior of copper and zinc metals in soil profile, submitted to different sources of fertilization

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Abstract

The application of high and continuous amounts of fertilizers to the soil can cause the accumulation of pollutants and biological agents, creating environmental and health problems. The objective of this work is to evaluate the presence and mobility within a soil profile of copper and zinc residual metals from chemical and organic fertilization after successive applications in three crops. The analysis was performed using X-ray fluorescence spectrometry. The experiment is conducted with a drainage lysimeter set. The soil used is a dystroferric Red Latosol, fertilized with chemical (nitrogen–phosphorus–potassium [NPK]) and organic (poultry litter and swine manure) fertilizers. Soil samples were collected from three points in each lysimeter at depths of 0–10, 10–20, 20–30, and 30–40 centimeters, dried in an oven, ground, and analyzed by dispersive energy X-ray fluorescence spectrometer. The copper and zinc elements from the successive applications of chemical and organic fertilization treatment accumulated in the soil profile. The use of the dispersive energy X-ray fluorescence spectrometer allowed the evaluation of the presence and mobility of the copper and zinc elements in the soil profile; however, the observed values do not indicate their availability.

KEYWORDS

metals in the soil, mobility, organic and chemical fertilization

1 | INTRODUCTION

In the southern region of Brazil, especially in the states of Rio Grande do Sul and Santa Catarina, swine farming is an activity commonly engaged in by small farms, with the waste produced by the swine used as fertilizer in areas with annual grains and pasture cultivation (Miele & de Miranda, 2013).

The great production of swine manure, coupled with practices involving the direct application of these wastes without any type of treatment, began to generate chemical, physical, and biological imbalances in the soil, the severity of which depends on the composition of the wastes and residues, the doses applied to each crop, plant extraction capacity, and soil type (Basso, Ceretta, de Moraes Flores, & Girotto, 2012).

Regions with high concentrations of pigs usually present serious environmental problems, mainly due to the characteristics of the residues produced from the wastes (da Silva, de França, & Oyamada, 2015). One example is the presence of heavy metals, many of which are toxic, even in small quantities, while others are harmful because they tend to accumulate due to the bioaffinity of living organisms (Basso et al., 2012).

Concern for contamination by metals in soil and water from the use of organic fertilizers (animal wastes) is primarily due to the presence of elements such as copper and zinc, which can cause alterations in the functionality and biological diversity of the soil. The contamination of the soil by metals, most of which are adsorbed to organic compounds, is an even greater problem, considering the difficulties in the quantitative determination of these contaminants and their variable behavior, which depends on their chemical structure, degradability, and bioactivity (Wuana & Okieimen, 2011).

Application of fertilizers that exceed crop demand may result in elevated levels of chemical elements, such as copper and zinc in the soil (Brunetto, Ferreira, Melo, Ceretta, & Toselli, 2017). The transport of heavy metals such as copper and zinc in the soil can occur as a result of the complexation with organic binders dissolved in solution, which may originate from the soil or from compounds added to the soil. These organic compounds can greatly increase the transfer of heavy metals by water runoff and percolation in the soil (Wuana & Okieimen, 2011).

Once adsorbed, the metals tend to accumulate in the roots, which are the first plant organs to be affected by soil contaminated by these elements, causing browning, thickening, and inhibition of root growth (Brunetto et al., 2017). The same authors report that in the aerial part

EXHIBIT 1 Chemical characteristics and clay content of the soil used in the experiment

Water pH	SMP	P	K	Al	Ca	Mg	Cu	Zn	H + Al	MO	Clay
--1:1--		--mg/L--		----------------Cmolc/L----------------						-----%-----	
6.1	6.1	4.6	46	0	11.3	3.6	12.9	12.8	3.3	2.9	36

Cmolc/L: centimoles per liter; mg/L: milligrams per liter; SMP: Shoemaker, MacLean, and Pratt method.

of the plants, the main symptoms are chloroses, similar to those indicative of deficiency of iron, and the appearance of spots of various forms, which evolve—or not—into leaf necrosis and death.

To reduce the potential risk of contamination from the use of animal waste, it is necessary to know the interactions between metals and soil, their distribution along the soil profile, and their availability to the plants, as this application practice requires care because of the great decomposition rate of organic matter in a tropical climate environment and the soil's ability to adsorb metals (Wuana & Okieimen, 2011).

In this context, the objective of this work is to evaluate the presence and mobility in a soil profile of copper and zinc residual metals from chemical and organic fertilization, after successive application in three crops, using X-ray fluorescence spectrometry.

2 | MATERIALS AND METHODS

The work was conducted in 2013 in the experimental area of the Center for Higher Education North-RS campus of the Federal University of Santa Maria in Frederico Westphalen, Rio Grande do Sul (RS), with geographic coordinates: latitude 27o 25′ 43″ S, longitude 53o 43′ 25″ W and average elevation of 488 meters (m) above mean sea level. The region's climate is humid subtropical, and the soil in the study area is classified as dystroferric Red Latosol (Streck et al., 2008, p. 222). The soil has been managed in the no tillage system for more than five years.

The physical and chemical characteristics of the soil layer (0, 0–20 centimeters [cm]), were determined three months before the implementation of the experiment and were obtained by the traditional methods of evaluation, which represent the availability of the elements in a soil fraction, are presented in the table in **Exhibit 1**.

In order to evaluate the presence of copper and zinc metals, the treatments used were: swine manure, poultry litter, and mineral fertilization (nitrogen–phosphorus–potassium [NPK]), in a set of drainage lysimeters. The set of lysimeters consists of 12 boxes made of fiberglass with dimensions of 1.40 × 1.00 m, and 1.00 m depth (**Exhibit 2**). This set of lysimeters is protected by a cover of ethylene vinyl acetate polyethylene supported by a metal structure.

In the lysimeter boxes, three previous cultivations, two of maize and one of oats, were conducted, and the recommended doses of NPK and organic fertilizers (mineral and swine and poultry litter fertilization) were applied for each treatment. Soil samples were collected before planting the fourth crop, black oats (*Avena strigosa*).

The soil samples were collected at three points in each lysimeter, and at each point four samples were collected at depths of 0–10, 10–20, 20–30, and 30–40 cm. After being collected, the soil samples were dried in a forced circulation oven at a temperature of 60 degrees Celsius for 24 hours and ground in a porcelain crucible for further analysis in the laboratory.

The analyses of the metals present (evaluation of the presence and not of the availability) in the soil were carried out in the Chemical Analysis and Research Laboratory (LAPAQ - CESNORS / UFSM), using a dispersive energy X-ray fluorescence spectrometer model Shimadzu EDX-720. The analytical method used is called the fundamental parameters method (Wastowski, da Rosa, Cherubin, & Rigon, 2010). This method allows researchers to obtain the sensitivity curve of the equipment for each element of interest, showing its presence in the soil and its volume in milligrams per kilogram (mg/kg).

For the analysis, approximately 0.5 grams of soil was used, conditioned under a 2.5 micrometer-thick Mylar® film stretched at the bottom of a polyethylene cell.

3 | RESULTS AND DISCUSSION

The table in **Exhibit 3** presents the mean values of the composition of the fertilizers used as the source of NPK and the average amount applied in the three previous crops. In this Exhibit, we verify that chemical fertilizing with urea, super triple phosphate (0–45–0 of the NPK mix), and potassium chloride, the observed values of copper and zinc present in this formula are considerable. For copper, we observed 58.8, 128.17, and 44.99 mg/kg, respectively, for the super triple, potassium chloride, and urea. However, the presence of zinc, with 359.54 mg/kg, was observed only in the super triple formulation. On the other hand, in the organic fertilizers (poultry litter and swine manure) the metals copper and zinc are present in quantities even greater than in the

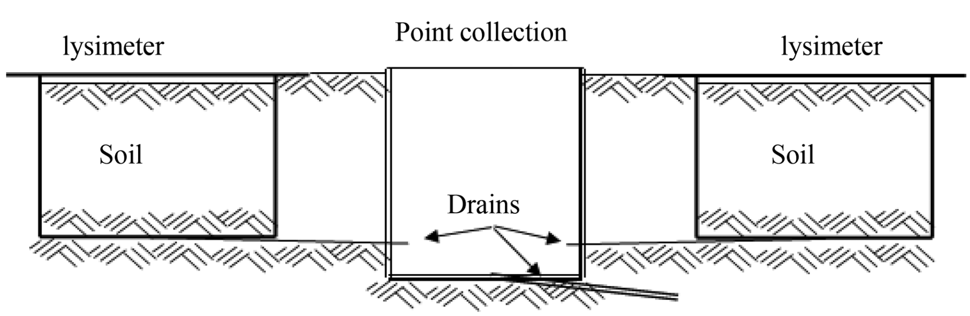

EXHIBIT 2 Outline diagram (profile schematic) of the drainage lysimeter assembly

EXHIBIT 3 Amount of copper (Cu) and zinc (Zn) present in the sources of chemical and organic fertilization and average amount of fertilization sources applied to the last three crops

Chemical elements	Amount present in fertilizer sources			Average amount applied to the three crops		
	Chemical fertilization (mg/kg)			Chemical fertilization (kg/ha)		
	Super triple	Potassium chloride	Urea	Super triple	Potassium chloride	Urea
Cu	58.80	128.17	44.99	1,101	1,098	552
Zn	359.54	0.00	0.00			
	Organic fertilization—swine manure			Organic fertilization—swine manure (kg/ha)		
Cu	313.74			15,471		
Zn	1,687.63					
	Organic fertilization—poultry litter			Organic fertilization—poultry litter (m^3/ha)		
Cu	308.96			157.5		
Zn	599.47					

kg/ha: kilograms per hectare; m^3/ha: cubic meters per hectare; mg/kg: milligrams per kilograms.

chemical fertilizers. The concentrations of copper and zinc found in the soil from fertilization with swine manure were observed as 313.74 mg/kg (for copper) and 1687.63 mg/kg (for zinc), while the concentrations from fertilization with poultry litter were observed as 308.96 mg/kg (for copper) and 599.47 kg/mg (for zinc). The presence of these metals in the formulations is justified by the addition of these metals in swine and chicken feed with the goal of preventing diseases, improving digestion, and promoting growth (Marcato & Lima, 2005).

The behavior of the accumulation of zinc in the soil as a function of the sampled depths of 0–10, 10–20, 20–30, and 30–40 cm can be observed in **Exhibit 4**, in soil fertilized with swine manure, poultry litter, and NPK. It is possible to verify that the zinc present in the fertilized soil accumulated within the soil profile by comparing the amounts shown in the treated soil to the profile of the control reference soil. These results corroborate those obtained by Basso et al. (2012) in areas of agriculture and pasture where swine manure was applied.

The treatment with mineral fertilization displayed the highest mobility of the zinc element in regard to depth, showing that the tendency of accumulation in the soil transverse to the depth of the horizons studied is similar to the behavior of the zinc in the control treatment (e.g., the soil that has not received an application of fertilizers). However, in the soil fertilized with poultry litter, the accumulation was greater at the surface, with concentrations of 76 mg/kg in the soil collected at 0–10 cm, while there was less accumulation in the soil collected at a depth of 20–30 cm, with a concentration of 45 mg/kg. The zinc accumulation in this treatment can be explained by the composition of chicken feeds, which have high amounts of iron and zinc, and it is common to observe high levels of these metals in poultry litter (Koiyama et al., 2014; Zhang, Li, Yang, & Li, 2012). High levels of these metals are observed in soils where there has been constant application of poultry residues for several years (Jackson et al., 2003).

In the soil fertilized with swine manure, the greatest accumulation of zinc was observed in the soil collected in the layer at a depth of 10–20 cm, with a concentration of 77 mg/kg. Similar results are found by Dal Bosco, Sampaio, Opazo, Gomes, and Nóbrega (2008), who wrote that when swine manure was applied to the ground, the greatest accumulation of zinc was observed in soil from the layer at a depth of 0–20 cm. These same authors affirm that this behavior can be related to the existence of the greater content of organic matter in the soil at the depth of 0–20 cm compared to the organic content found at a depth of 20–40 cm because, according to Bertol (2005), the organic matter displays a capability of immobilizing metals that are present in the soil by means of the adsorption of these elements by the different components of the organic matter.

The tendency of accumulation of zinc shown in **Exhibit 4** justifies itself in the treatments where organic fertilizer was used, as zinc, as well as copper, are important components in the formulation of animal feeds. According to Basso et al. (2012), when zinc and copper are applied to the soil, they can be fixed in the soil's organic fraction and temporarily immobilized by the microorganisms. Much of the zinc available in mineral soils is associated with the amount of organic matter present. Thus, low levels of organic matter in mineral soils are often

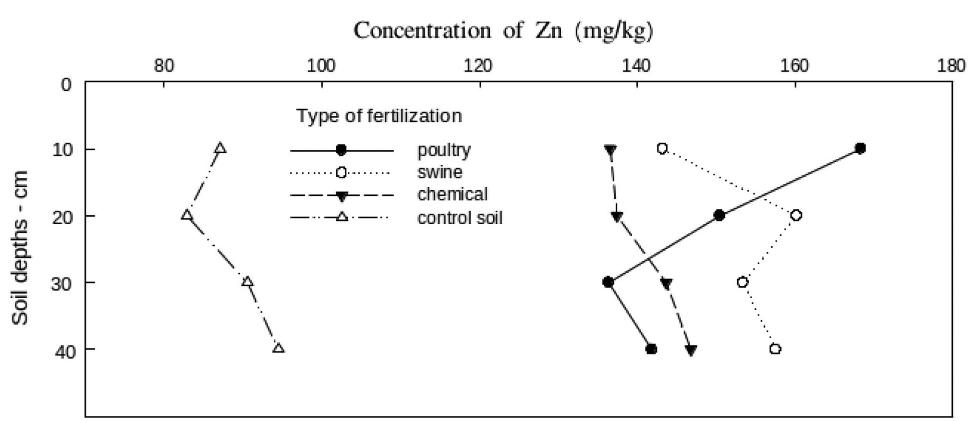

EXHIBIT 4 Concentration of zinc (Zn) at different soil depths, fertilized with swine manure, poultry litter, and chemical fertilizer (nitrogen–phosphorus–potassium [NPK])
cm: centimeters; mg/kg: milligrams per kilograms.

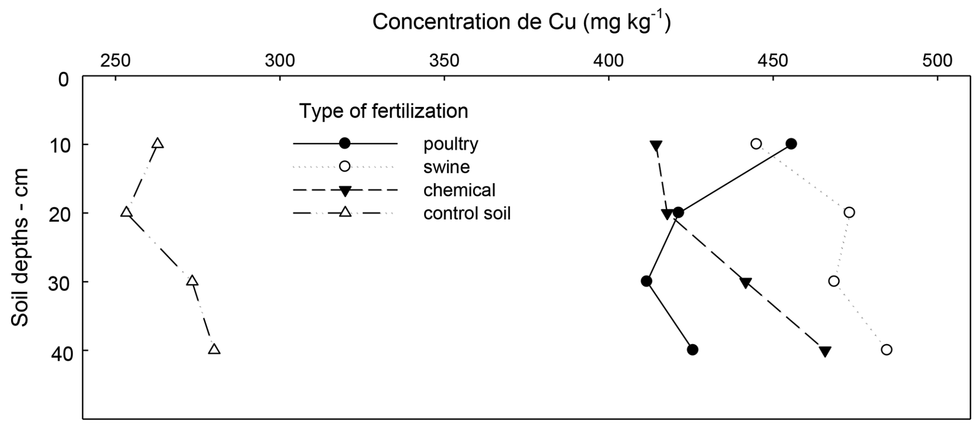

EXHIBIT 5 Concentration of copper (Cu) at different depths of the soil, fertilized with swine manure, poultry litter, and chemical fertilization (nitrogen–phosphorus–potassium [NPK])

indicative of low availability of zinc (Paganini, Souza, and Bocchiglieri, 2004). On the other hand, excess zinc affects the root growth of plants (White & Broadley, 2009).

Exhibit 5 presents the behavior of copper accumulation in the soil profile at depths of 0–10, 10–20, 20–30, and 30–40 cm in soil fertilized with swine manure, poultry litter, and NPK. The copper accumulation tendency in all treatments is compared to the control treatment. Soil fertilized with swine manure and NPK showed higher copper accumulations in samples taken from depths of 30–40 cm deep of 440 and 463 mg/kg, respectively, while in soil fertilized with poultry litter, the highest concentration was observed on the surface (0–10 cm) with 455 mg/kg.

In soils treated with swine manure, the element copper had a higher accumulation 490 mg/kg at the 30–40 cm deep layer than at shallower depths. These results corroborate those found by Dal Bosco et al. (2008), which obtained higher concentrations of copper in the soil at depths of 20–40 cm. The characterization of higher concentrations of copper at greater depths of the soil also creates concern, as the presence of these concentration levels could allow for the contamination of the groundwater.

From the analysis of Exhibits 4 and 5 it can be observed that successive applications of fertilizer, both chemical and organic, showed a tendency to cause the accumulation of copper and zinc in the soil profile. In addition, along with the accumulation of such metals, there is mobility toward the deeper layers of the soil profile. The higher or lower mobility of metals is determined by soil attributes, such as clay content and type, pH, cations exchange capacity, and organic matter content, all of which influence the adsorption, precipitation/dissolution, complexation, and oxidation and reduction of metals (Pierangeli, Guilherme, Curi, Anderson, & Lima, 2004).

4 | CONCLUSION

The use of the dispersive energy X-ray fluorescence spectrometer allowed the evaluation of the presence and mobility of the copper and zinc elements in the soil profile; however, these observed values do not indicate their availability.

The copper and zinc elements from the successive application of chemical and organic fertilization treatments accumulated in the soil profile. The soil receiving fertilization with swine manure and poultry litter showed higher accumulations of copper and zinc in the surface layer compared to the accumulations shown in chemical fertilization treatment. The zinc element was more mobile in treatments with organic fertilization. Treatment with swine manure provided the largest accumulations of copper and zinc elements at depth in the soil.

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